Quantum description of the orientational degrees of freedom in a biaxial nematic liquid

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Abstract

The quantum mechanical version of a classical model for studying the orientational degrees of freedom corresponding to a nematic liquid composed of biaxial molecules is presented. The effective degrees of freedom are described by operators carrying an $SU(3)$ representation, which allows the explicit calculation of the partition function in the mean field approximation. The algebraic consistency conditions are solved numerically and the equilibrium phases of the system are determined. In particular, the entropy, the specific heat and the order parameters are presented for different choices of the constituent biaxial molecules. Our results reproduce the classical calculation in the limit of high temperatures and high quantum numbers.

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1 Introduction

Nematic liquids constitute a particular case of the phases denominated with the generic name of liquid crystals [1, 2]. This is a state of matter which is intermediate between the liquid and the solid phases. It lacks the positional symmetry characterizing the lattice of a crystal, which makes it similar to a liquid, but it retains some orientational symmetry that is not present in a normal (isotropic) liquid. The molecules forming a liquid crystal can be roughly caracterized as rod-like or disc-like, and the corresponding orientational symmetry is manifested by different types of local aligments of such molecules with respect to a preferred direction characterized by a unit vector called the director. In the case of a nematic liquid, the director is fixed in space and the molecules remain, on the average, parallel to it, though they can difuse as in a normal liquid. The existence of a preferred direction makes this phase to exhibit birrefringent properties. On the other hand, the energies involved in the transition from the liquid crystal phase to the isotropic liquid phase are normally small compared with the corresponding ones in the solid-liquid transition. This makes it possible to drastically change the response of liquid crystals by external agents, using relatively small amounts of energy. It is this property which determines the numerous and important technological applications of liquid crystals [3].

Besides the important applications of liquid crystals in everyday's life, together with the huge amount of theoretical work that has been consequently developped, it has been suggested recently that these phases might be relevant also in other situations, like for example, the description of nuclear matter under very stringent conditions of densities and temperatures [4], particularly in the case of neutron stars. These quantum objects are cold stars composed primarily of neutrons and supported against collapse by neutron degeneracy pressure. In this situation, it is predicted that the inner crust of a neutron star (roughly located at 9.2 km from the center of a typical neutron star with a radious of 10 km and a mass of 1.5 solar masses) is separated from the core, composed mainly of uniform nuclear matter, by a thin spherical shell about 0.1 km wide, containing nuclear matter in the form of non-spherical nuclei (rods, plates, tubes) plus dripped neutrons plus electrons. This liquid crystal behavior, as opposed to a crystalline solid, will have important consequences for a number of aspects of neutron star properties [5]. Nevertheless, there is a main difference between this case and the situation in the laboratory: in the neutron star case, the basic entities from which nuclei are constructed are nucleons, which are spherical; while in laboratory liquid crystals, the basic ingredientes are non-spherical biaxial molecules in general [5]. In this respect, it might be interesting to consider liquid crystals made up from constituentes having permanent magnetic moments, as nucleons, generating a liquid ferromagnet. In the laboratory, such structures, though not forbidden, should be very rare because the exchange couplings beteween neighboring magnetic moments are much weaker than the conventional interactions between molecules.

Motivated by some of the above considerations, we consider the quantum mechanical description of the orientational degrees of freedom of a nematic liquid consisting of biaxial molecules, in the mean field approximation. This system has been previously discussed in

Ref.[6], where an exact calculation of the classical partition function, together with an extensive analysis of the corresponding phases, transition temperatures, themodynamic quantities and order parameters, was made. We will refer to this work as the classical model. In this reference, the effective orientational degrees of freedom of the non-spherically symmetric molecules were described by an $SU(3)$ invariant Hamiltonian constructed from the angular momentum operators L_i, $i = 1, 2, 3$ together with the traceless quadrupole tensor operator $Q_{\alpha\beta}$, $\alpha, \beta = 1, 2, 3$, which constitute a representation for the generators of $SU(3)$. The interpretation of the model was performed in a coordinate system where the molecule is at rest, i.e. $L_i = 0$. In this system, the quadrupole operator $\bar{Q}_{\alpha\beta}$ relates to the inertia tensor of the molecule in such a way that the $SU(3)$ Casimir operators, related to the eigenvalues of $\bar{Q}_{\alpha\beta}$, provide a description of the shape of the molecule.

The classical partition function in the mean field approximation was exactly calculated in Ref.[6] by first rewritting it as an integral over the space parameters of the $SU(3)$ group, according to a theorem due to Macfarlane et al. [7]. This integral has been previously calculated in the bosonic case by Harish-Chandra, and Itzykson and Zuber [8]. The exact evaluation of the partition function, together with the fact that the consistency conditions consisted in two coupled algebraic equations, constituted an advantage over previous statistical theories proposed [9] in order to explain the isotropic $\rightarrow$ uniaxial $\rightarrow$ biaxial phase transitions discovered experimentally in nematic liquids [10]. The works included in [9] are generalizations of the Maier-Saupe theory, that was for some time the fullest existing statistical mechanical theory of the nematic state, which, nevertheless, did not include the biaxial phase [11].

Following an approach similar to some previous works, we only consider the orientational interaction energy among the molecules of the liquid, in such a way that the exact nature of the intermolecular forces need not be specified . Whether the liquid crystal state arises because of the hard core repulsive forces or the long range dispersive forces is a matter of indifference in the following. This approximation is expected to produce qualitatively reasonable results in the nematic case [9]. In this way, we are really calculating the excess thermodynamical properties of the ordered system, relative to those of the disordered one.

In this work we present a quantum description of the problem discussed in [6], which amounts to the generalization of the usual Heisenberg model describing the interaction of angular momentum operators ($SU(2)$ case) to the situation where the interacting operators carry an $SU(3)$ representation. Similarly to the classical case, we are able to exactly calculate the partition function in the mean field approximation. This is achieved by using the Weyl formula for the characters of $SU(3)$ [12]. We expect to recover the results of Ref.[6] in the high temperature, high quantum numbers limit [13, 14].

The paper is organized as follows. In section 2 we introduce the model and apply the Weyl formula to calculate the partition function. Section 3 describes the characterization of the constituents molecules of the liquid in terms of the irreducible representations of $SU(3)$. The equilibrium phase is parametrized in the same way as in Ref. [6] as briefly recalled in section 4. The connection with the classical case is presented in section 5, where a function relating the corresponding partitions functions is explicitly calculated. Section 6 contains

the selfconsistent equations that allow for a numerical determination of the equilibrium parameters, which are obtained by determining the absolute mimima of the free energy of the system. Besides, some symmetry properties of the quantum partition function are exhibited there. Section 7 describes the calculation of the equilibrium parameters of the different phases of the system, emphasizing those limiting cases that can be treated algebraically. We have also calculated numerically the specific heat and the entropy as functions of the adimensional temperature, for some representative cases. The order parameters in the quantum case are also defined in this section. In many of the figures presented, we have shown both the classical and quantum predictions in order to assess the main differences between the two approaches. Some conclusions and comments are presented in section 9. Finally, there is an Appendix summarizing some basic properties of $SU(3)$. Here we also give an alternative way of rewritting the partition function, in terms of polynomials, which have been useful in obtaining some limiting cases considered along this work.

2　The model

Following the work of Ref. [6], let us consider the effective Hamiltonian

$$H = -\frac{J}{N} \sum_{m \neq n} S_a^m S_a^n, \tag{1}$$

which describes the orientational energy of the system. Here, the N independent operators S_a^m, $m = 1, 2, 3, \ldots, N$, $a = 1, 2, 3, \ldots, 8$ describe the degrees of freedom of each molecule of the liquid and carry an $SU(3)$ representation, i.e.

$$[S_a^m, \ S_b^n] = \delta^{mn} i f_{abc} \ S_c^m, \tag{2}$$

where f_{abc} are the $SU(3)$ structure constants. As it is well known, the fundamental representation of this group is written in terms of the Gell-Mann 3×3 matrices λ_a given in the Appendix, where other useful properties are also recalled.

In the mean field (molecular field) aproximation we replace (1) by

$$H = -JB_a \sum_n S_a^n, \tag{3}$$

where the eight-dimensional vector $B_a = \frac{1}{N} < \sum_m S_a^m >$, which represents the average field seen by each molecule, has to be determined consistently.

In this approximation, the partition function Z is

$$Z = Tre^{-\beta H} = Tre^{\beta J B_a \sum_{n=1}^{N} S_a^n} = Z_0^N, \tag{4}$$

where

$$Z_0 = Tre^{\beta J B_a S_a}. \tag{5}$$

As usual $\frac{1}{\beta} = kT$, where k is the Boltzman constant and T is the temperature of the system.

The consistency equations for the mean field approximation reduce to

$$B_a = \frac{1}{\beta J} \frac{\partial}{\partial B_a} ln Z_0. \tag{6}$$

The basic problem now is to calculate such partition function for an arbitrary (p, q) irreducible representation of $SU(3)$. The first step is to select and adequate coordinate system to perform the calculation. Since the trace is invariant under a unitary transformation of the operator inside, we can diagonalize the hermitian operator $\beta J B_a S_a$ in such a way that it can be written as $\beta J(B_3 S_3 + B_8 S_8)$, where we assume that the operators S_3 and S_8 are chosen to be simultaneously diagonal. This is equivalent to choose a coordinate system where the eight-dimensional vector B_a has only non-zero components in the 3 and 8 axis. The fact that we need two non-zero components, instead of one as in the $SU(2)$ case, is related to the property that in the adjoint representation of $SU(3)$ there are two invariants: $B_a B_a$ and $d_{abc} B_a B_b B_c$. Using the explicit form of d_{abc}, it can be shown that it is possible to select the B_3 and B_8 components as the only non-zero ones. In this way we are left with

$$Z_0 = Tr e^{\beta J(B_3 S_3 + B_8 S_8)}. \tag{7}$$

From now on we will assume that $B_a = (0, 0, B_3, 0, \ldots, B_8)$.

In the fundamental representation $(1, 0)$, the partition function is given by

$$Z_0 = \sum_i e^{\beta J \vec{B} \cdot \vec{\mu}_i}, \tag{8}$$

where $\vec{\mu}_i$ are the weights of the fundamental representation.

The partition function (5) is the character of the operator $e^{-\beta H}$. In this way, to calculate Z_0 for an arbitrary representation (p, q) of $SU(3)$, we can use the Weyl formula for the characters of $SU(n)$, given in terms of the eigenvalues of the operator in the fundamental representation. For $SU(3)$, the Weyl formula reduces to [12]

$$Z_0 \equiv \Sigma^{\{\eta_1, \eta_2\}} = \frac{1}{(\Lambda_1 - \Lambda_2)(\Lambda_1 - \Lambda_3)(\Lambda_2 - \Lambda_3)} \begin{vmatrix} \Lambda_1^{\eta_1+2} & \Lambda_1^{\eta_2+1} & 1 \\ \Lambda_2^{\eta_1+2} & \Lambda_2^{\eta_2+1} & 1 \\ \Lambda_3^{\eta_1+2} & \Lambda_3^{\eta_2+1} & 1 \end{vmatrix}. \tag{9}$$

Here $\eta_1 = p + q$ is the number of boxes in the first row of the corresponding Young tableau, while $\eta_2 = q$ is the number of boxes in the second row of the tableau. In other words, p is the number of columns with one box ($p \geq 0$) and q is the number of columns with two boxes ($q \geq 0$) in the tableau. The representation $(0, 0)$ is the trivial one. The eigenvalues Λ_i, $i = 1, 2, 3$ are given by

$$\Lambda_i = e^{\beta J \vec{B} \cdot \vec{\mu}_i} \tag{10}$$

and satisfy the condition $\Lambda_1 \Lambda_2 \Lambda_3 = 1$. The weights $\vec{\mu}_i$ are given in the Appendix.

4

A more convenient notation is

$$\rho = \frac{1}{2}\beta J B_3, \quad \sigma = \frac{1}{2\sqrt{3}}\beta J B_8, \tag{11}$$

which produces the following expressions for the eigenvalues of the Hamiltonian in the fundamental representation

$$\Lambda_1 = e^{\rho+\sigma}, \quad \Lambda_2 = e^{-\rho+\sigma}, \quad \Lambda_3^{-1} = \Lambda_1\Lambda_2 = e^{2\sigma}. \tag{12}$$

The partition function is given by

$$
\begin{aligned}
Z_0^{(p,q)} &= \frac{1}{\sinh 2\rho - 2\sinh\rho\cosh 3\sigma}\left(-e^{(p+2q+3)\sigma}\ \sinh(p+1)\rho\right. \\
&\quad \left.+e^{(p-q)\sigma}\ \sinh(p+q+2)\rho - e^{-(q+2p+3)\sigma}\ \sinh(q+1)\rho\right).
\end{aligned}
\tag{13}
$$

It is convenient to observe that the above expression for $Z_0^{(p,q)}$ can be rewritten as

$$Z_0^{(p,q)} = \frac{N^{(p,q)}}{N^{(0,0)}}, \tag{14}$$

where

$$
\begin{aligned}
N^{(p,q)} &= e^{(p-q)\sigma}\ \sinh(p+q+2)\rho - e^{(p+2q+3)\sigma}\ \sinh(p+1)\rho \\
&\quad - e^{-(q+2p+3)\sigma}\ \sinh(q+1)\rho.
\end{aligned}
\tag{15}
$$

3   Specification of the constituent molecules

The orientational degrees of freedom of the molecules are described by the eight operators S_a, which can be reinterpreted as the angular momentum L_i, $i = 1, 2, 3$ and the quadrupole moment Q_{ij} operators, according to [6],

$$
\begin{aligned}
&L_1 = 2S_7, \quad L_2 = -2S_5 \quad L_3 = 2S_2, \\
&Q_{12} = S_1, \quad Q_{13} = S_4, \quad Q_{23} = S_6, \\
&Q_{11} = S_3 + \frac{1}{\sqrt{3}}S_8, \quad Q_{22} = -S_3 + \frac{1}{\sqrt{3}}S_8, \quad Q_{33} = -\frac{2}{\sqrt{3}}S_8.
\end{aligned}
\tag{16}
$$

The molecules forming the liquid will be characterized by the representation (p, q) of $SU(3)$. To this end we consider the two Casimir operators of the group

$$\mathbf{C_2} = S_a S_a = I_2\mathbf{I}, \qquad \mathbf{C_3} = d_{abc}S_a S_b S_c = I_3\mathbf{I} \tag{17}$$

which take the following values in each irreducible representation (p, q), [15]

$$I_2 = \frac{p^2 + q^2 + pq + 3(p + q)}{3},\tag{18}$$

$$I_3 = \frac{1}{18}(p - q)(p + 2q + 3)(2p + q + 3).\tag{19}$$

Motivated by the classical description and in order to compare with it, we introduce a parametrization of the above invariants in terms of μ_i, $i = 1, 2, 3$, with the restriction $\mu_1 + \mu_2 + \mu_3 = 0$. In the classical case one defines $I_3 = \frac{3}{2}\mu_1\mu_2\mu_3$, which can be reproduced in our case by choosing

$$\mu_1 = -\frac{1}{3}(p + 2q + 3), \quad \mu_2 = -\frac{1}{3}(p - q), \quad \mu_3 = \frac{1}{3}(2p + q + 3),\tag{20}$$

according to the relation (19). Following the analogy, we next calculate what used to be the quadratic Casimir operator. We obtain

$$-(\mu_1\mu_2 + \mu_1\mu_3 + \mu_2\mu_3) = I_2 + 1,\tag{21}$$

where I_2 is given by Eq.(18).

The choice (20) implies the ordering $\mu_1 \leq \mu_2 \leq \mu_3$, for arbitrary values of p and q.

The eigenvalues (20) satisfy the cubic equation

$$\mu^3 - (I_2 + 1)\mu - \frac{2}{3}I_3 = 0,\tag{22}$$

and can be parametrized as

$$\mu_1 = \mu \cos\left(\psi + \frac{2\pi}{3}\right), \quad \mu_2 = \mu \cos\left(\psi - \frac{2\pi}{3}\right), \quad \mu_3 = \mu \cos\psi,\tag{23}$$

which is consistent with the ordering introduced in (20). To this end we must always have

$$\mu \sin\psi > 0, \quad \mu \cos\psi > 0, \quad \tan\psi \leq \sqrt{3},\tag{24}$$

where

$$\mu = \pm 2\sqrt{\frac{(I_2 + 1)}{3}}, \quad \cos 3\psi = \pm\frac{\sqrt{3}I_3}{(I_2 + 1)^{\frac{3}{2}}},\tag{25}$$

in complete analogy with the classical case. The above conditions lead to the following correlations between ψ and μ

$$\mu > 0 \leftrightarrow 0 < \psi < \frac{\pi}{3}, \quad \mu < 0 \leftrightarrow \pi < \psi < \pi + \frac{\pi}{3},\tag{26}$$

for arbitrary p and q. In this way, for p and q fixed, the change $\mu \to -\mu$ has to be followed by $\psi \to \psi + \pi$. Thus we pass from the upper plus sign to the lower minus sign in the two relations contained in (25).

6

The physical interpretation associated to the (p, q) characterization of the individual molecules is made through the classical connection

$$a_i{}^2 = \frac{1}{3}(a_1{}^2 + a_2{}^2 + a_3{}^2) + \frac{1}{2}\mu_i,\tag{27}$$

which relates the μ-values (20) with the shape corresponding to a molecule described by a mass distribution defined by six equal masses at distances $\pm a_1, \pm a_2, \pm a_3$ from the center [6]. Here we are assuming that the a_i's are written in dimensionless units. The correspondence is

$$\mu_1 = \mu_2 = \mu_3 \quad \text{(spherically symmetric molecule)},$$
$$\mu_1 = \mu_2 < 0, \quad \mu_3 > 0, \quad \text{(rod molecule)},$$
$$\mu_1 < 0, \quad \mu_2 = \mu_3 > 0, \quad \text{(disc molecule)},$$
$$\frac{1}{2}(\mu_1 + \mu_3) > \mu_2, \quad \text{(rod−like molecule)},$$
$$\frac{1}{2}(\mu_1 + \mu_3) < \mu_2, \quad \text{(disc−like molecule)}.\tag{28}$$

The expressions (20) together with the classification (28), imply that in the quantum case we do not have at our disposal either spherically symmetric or uniaxial molecules to begin with. The description used allows only biaxial molecules which are rod-like $(p > q)$ or disc-like $(p < q)$.

Using the parametrization (23) we obtain the following expressions for the functions of p, q appearing in the partition function (13)

$$-\frac{1}{3}(p - q) = \mu \cos(\psi - \frac{2\pi}{3}), \quad -\frac{1}{\sqrt{3}}(p + q + 2) = \mu \sin(\psi - \frac{2\pi}{3}),$$
$$-\frac{1}{3}(p + 2q + 3) = \mu \cos(\psi + \frac{2\pi}{3}), \quad \frac{1}{\sqrt{3}}(p + 1) = \mu \sin(\psi + \frac{2\pi}{3}),$$
$$+\frac{1}{3}(2p + q + 3) = \mu \cos\psi, \quad \frac{1}{\sqrt{3}}(q + 1) = \mu \sin\psi.\tag{29}$$

4 Parametrization of the equilibrium phases

The equilibrium state of the system is characterized by the vector B_a in the frame where its only components are B_3 and B_8. Again, an $SU(3)$ invariant description of such phase will be given by the corresponding vector invariants, in the adjoint representation

$$\bar{I}_2 = B_a B_a = B_3{}^2 + B_8{}^2, \quad \bar{I}_3 = d_{abc} B_a B_b B_c = \frac{1}{\sqrt{3}}(-B_8{}^3 + 3B_8 B_3{}^2).\tag{30}$$

These invariants take continuous values as opposed to those describing the individual molecules, which have only discrete values.

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From Eqs (30), we can verify that B_8 satisfies the cubic equation

$$B_8{}^3 - \bar{I}_2 B_8 - \frac{2}{3}\bar{I}_3 = 0 \tag{31}$$

and consequently can be parametrized in any of the forms (23). A convenient choice is made by considering that the relevant variable is the matrix $B_a \lambda_a$ in the fundamental representation, which eigenvalues are

$$\vec{\mu}_1 \cdot \vec{B} = \lambda_1 = \frac{1}{2}B_3 + \frac{1}{2\sqrt{3}}B_8 := \lambda \cos\left(\phi + \frac{2\pi}{3}\right),$$

$$\vec{\mu}_2 \cdot \vec{B} = \lambda_2 = -\frac{1}{2}B_3 + \frac{1}{2\sqrt{3}}B_8 := \lambda \cos\left(\phi - \frac{2\pi}{3}\right),$$

$$\vec{\mu}_3 \cdot \vec{B} = \lambda_3 = -\frac{1}{\sqrt{3}}B_8 := \lambda \cos\phi. \tag{32}$$

In this way we identify

$$B_8 = -\sqrt{3}\,\lambda\,\cos\phi, \qquad B_3 = -\sqrt{3}\,\lambda\,\sin\phi. \tag{33}$$

The equilibrium phase is described by the variables λ, ϕ, which can be translated in a geometrical language regarding the average shape of the equilibrium states via the relations (28) and (32), in terms of the eigenvalues λ_i.

5   Connection with the classical case

The parametrization (29) allows us to rewrite the quantum partition function in a form that closely resembles the classical case. In fact, the factor $N^{(p,q)}$ of $Z_0^{(p,q)}$, given in Eq. (15), can be rewritten as

$$N^{(p,q)} = \frac{1}{2}A(X, \phi - \psi) - \frac{1}{2}A(X, \phi + \psi) = \frac{1}{2}D(X, \phi, \psi), \tag{34}$$

where $X = \frac{\sqrt{3}}{2}\mu y$ and $D(X, \phi, \psi)$ is the same expression as in the classical case, since we have

$$A(X, \alpha) = \mathrm{e}^{X\cos\alpha} + \mathrm{e}^{X\cos(\alpha - \frac{2\pi}{3})} + \mathrm{e}^{X\cos(\alpha + \frac{2\pi}{3})}. \tag{35}$$

Here we have introduced the following dimensionless variables

$$T = \frac{4}{\beta J}, \quad y = \frac{4\sqrt{3}}{T}\lambda, \quad \rho = -\frac{y}{2}\sin\phi, \quad \sigma = -\frac{y}{2\sqrt{3}}\cos\phi. \tag{36}$$

The temperatute T_c used in Ref. [6] is related to our definition by

$$T_c = \frac{1}{3\mu^2}T, \tag{37}$$

8

where μ is given by Eq.(25). In the sequel we will refer to T_c as the classical temperature.

The denominator of the partition function can also be written as

$$N^{(0,0)} = -4 \sinh(\frac{y}{2}\sin\phi) \sinh(\frac{y}{2}\sin(\phi - \frac{2\pi}{3})) \sinh(\frac{y}{2}\sin(\phi + \frac{2\pi}{3})), \qquad (38)$$

which allows a more direct comparison with the classical case.

In fact, in the limit $T \to \infty$ $(y \to 0, X \to 0)$ the above expression reduces to

$$N^{(0,0)} = -\frac{1}{2}y^3 \sin\phi \sin(\phi - \frac{2\pi}{3}) \sin(\phi + \frac{2\pi}{3}) = \frac{1}{8}y^3 \sin3\phi. \qquad (39)$$

Since in the case $p = q = 0$ we have $\mu = \frac{2}{\sqrt{3}}$, $y = X$, $I_3 = I_2 = 0$, $\sin3\psi = 1$, we can write $N^{(0,0)} = \frac{1}{8} X^3 \sin3\phi \sin3\psi$. Then, in this limit we have

$$Z_0^{(p,q)}|_{T\to\infty} = \frac{4D(X, \phi, \psi)}{X^3 \sin3\phi \sin3\psi}. \qquad (40)$$

In order to compare the full quantum partition function with its classical counter part, we subsequently make a precise connection between the two approaches, by rewriting the variable $x_c = \frac{3}{2}\lambda_c\mu_c$ used in [6], in our terms. Here μ_c denotes the "radius" in the parametrization of the constituent phase eigenvalues, and $\mu_c = \mu_q$, according to Eqs.(20). The subindices c, q refer to the classical [6] and quantum cases, respectively. The value λ_c is the "radius" of the parametrization of the equilibrium phase, given by the eigenvalues λ_i in Ref [6]. The variable $\bar{S}_a$ of Ref. [6] is what we call B_a and the matrix whose eigenvalues are the λ_i's is $M_1 = \frac{\beta J}{2}B_a(2\lambda_a)$, where we have used that $(\lambda_a)_c = 2(\lambda_a)_q$. We have labeled the "radius" associated to the parametrization of the eigenvalues of $B_a\lambda_a$ by $\lambda_q = \frac{y}{\sqrt{3}\beta J}$ in such a way that $\lambda_c = \beta J\lambda_q$. Then we obtain $x_c = \frac{3}{2}\beta J\lambda_q\mu_q$. On the other hand, we have that $X = \frac{\sqrt{3}}{2}\mu_q$ $y = \frac{3}{2}\beta J\lambda_q\mu_q = x_c$. In this way, (40) is exactly the partition function given in Ref [6].

Thus, we can readily see that the numerator of our quantum partition function (14) coincides with the classical case, except for the fact that the angle ψ is rectricted to discrete values according to the relations (18), (19), (25), (20) and (23). The denominator is quite different from the classical case and shows no dependence upon the angle ψ, i.e. upon the input parameters p, q.

In general, we can relate the quantum $(Z_0^{(p,q)})$ and classical $((Z_0)_c = Q)$ partition functions by

$$Z_0 = \mathcal{Z} Q, \qquad (41)$$

with

$$\mathcal{Z} = D^{(p,q)}\frac{\frac{y}{2}\sin\phi}{\sinh(\frac{y}{2}\sin\phi)} \frac{\frac{y}{2}\sin(\frac{2\pi}{3} - \phi)}{\sinh(\frac{y}{2}\sin(\frac{2\pi}{3} - \phi))} \frac{\frac{y}{2}\sin(\frac{2\pi}{3} + \phi)}{\sinh(\frac{y}{2}\sin(\frac{2\pi}{3} + \phi))}, \qquad (42)$$

where $D^{(p,q)}$ is de dimension of the (p, q) representation of $SU(3)$. Let us observe that the quantum calculation depends upon the parameter μ, as opposed to the classical case where this variable appears only through the combination x_c.

6 Calculation of the equilibrium parameters

In the coordinates chosen so far, the consistency equations in the mean field approximation are given by

$$B_3 = \frac{1}{\beta J} \frac{\partial}{\partial B_3} \ln Z_0^{(p,q)}, \quad B_8 = \frac{1}{\beta J} \frac{\partial}{\partial B_8} \ln Z_0^{(p,q)}, \tag{43}$$

where the partition function $Z_0^{(p,q)}$ is written in Eq.(13). The original expression

$$B_a = \frac{1}{Z_0} Tr \left(S_a e^{\beta J(B_3 S_3 + B_8 S_8)} \right), \quad a = 3, 8, \tag{44}$$

for the consistency conditions, allows us to see that we will always have the solution $B_3 = 0 = B_8$, ($\lambda = y = 0$) corresponding to the isotropic phase. In this case, the partition function is $Z_0 = D^{(p,q)}$, independent of the variable ϕ, which we choose as $\phi = 0$ to describe the isotropic phase. Nevertheless, this phase will not always be the stable one.

Changing to the variables λ, ϕ introduced in Eq.(33), the equilibrium equations reduce to

$$\lambda = \frac{1}{3\beta J} \frac{\partial}{\partial \lambda} \ln Z_0^{(p,q)}, \quad \frac{\partial}{\partial \phi} \ln Z_0^{(p,q)} = 0, \tag{45}$$

which can be rewritten as

$$\frac{1}{4} y \, T = \frac{\partial}{\partial y} \ln Z_0^{(p,q)}, \quad 0 = \frac{\partial}{\partial \phi} \ln Z_0^{(p,q)}, \tag{46}$$

in terms of the variables defined in Eq.(36).

The free energy F of the system is

$$\beta F = -\ln Z_0^{(p,q)} + \frac{T}{2}\rho^2 + \frac{3T}{2}\sigma^2 = -\ln Z_0^{(p,q)} + \frac{1}{8} \, T y^2, \tag{47}$$

which has to be an absolute local minimum, according to Eqs. (46), in order to determine the equilibrium state of the system.

The thermodynamic properties are given by

$$\frac{S}{k} = -\frac{1}{4} y^2 \, T + \ln Z_0^{(p,q)}, \quad \frac{U}{J} = -\frac{1}{32} T^2 y^2, \quad \frac{C}{k} = -\frac{1}{8} \frac{d}{dT} (y^2 T^2), \tag{48}$$

where S is the entropy per particle due to the orientational order, U is the energy per particle and C is the specific heat. They correspond to the same expressions used in Ref. [6].

In order to study the symmetries of the partition function $Z_0^{(p,q)}$ it is convenient to rewrite it as

$$Z_0^{(p,q)} = \frac{1}{(\Lambda_1 - \Lambda_2)(\Lambda_1 - \Lambda_3)(\Lambda_2 - \Lambda_3)} \begin{vmatrix} \Lambda_1^{-(q+1)} & \Lambda_1^{(p+1)} & 1 \\ \Lambda_2^{-(q+1)} & \Lambda_2^{(p+1)} & 1 \\ \Lambda_3^{-(q+1)} & \Lambda_3^{(p+1)} & 1 \end{vmatrix}, \tag{49}$$

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together with

$$\Lambda_1 = e^{\frac{1}{\sqrt{3}}\, y\cos\left(\phi+\frac{2\pi}{3}\right)}, \quad \Lambda_2 = e^{\frac{1}{\sqrt{3}}\, y\cos\left(\phi-\frac{2\pi}{3}\right)}, \quad \Lambda_3 = e^{\frac{1}{\sqrt{3}}\, y\cos\phi}, \tag{50}$$

according to Eqs. (10), (32) and (36). The partition function is invariant under each of the following separate set of transformations, which do not change the system under consideration

$$y \to y, \quad \phi \to -\phi, \qquad (\Lambda_1 \leftrightarrow \Lambda_2, \quad \Lambda_3 \to \Lambda_3), \tag{51}$$

$$y \to y, \quad \phi \to \frac{2\pi}{3} - \phi, \quad (\Lambda_3 \leftrightarrow \Lambda_2, \quad \Lambda_1 \to \Lambda_1), \tag{52}$$

$$y \to y, \quad \phi \to \frac{4\pi}{3} - \phi, \quad (\Lambda_3 \leftrightarrow \Lambda_1, \quad \Lambda_2 \to \Lambda_2) \tag{53}$$

$$y \to y, \quad \phi \to \phi - \frac{2\pi}{3}, \quad (\Lambda_1 \to \Lambda_3 \to \Lambda_2 \to \Lambda_1) \tag{54}$$

$$y \to y, \quad \phi \to \phi + \frac{2\pi}{3}, \quad (\Lambda_1 \to \Lambda_2 \to \Lambda_3 \to \Lambda_1). \tag{55}$$

The above set of transformations allow us to restrict the initial interval $-\pi < \phi < \pi$ to $0 < \phi < \frac{\pi}{3}$. Furthermore, we have the following relations among the different values of Λ_i

$$\begin{aligned} 0 < \Lambda_1 < \Lambda_2 < 1 < \Lambda_3, \quad & 0 < \phi < \frac{\pi}{6}, \\ 0 < \Lambda_1 < 1 < \Lambda_2 < \Lambda_3, \quad & \frac{\pi}{6} < \phi < \frac{\pi}{3}. \end{aligned} \tag{56}$$

The remaining symmetries exchange rod-like into disc-like phases

$$p \leftrightarrow q, \quad y \to y, \quad \phi \to \pi - \phi, \quad \left(\Lambda_1 \leftrightarrow \Lambda_2{}^{-1}, \quad \Lambda_3 \to \Lambda_3{}^{-1}\right), \tag{57}$$

$$p \leftrightarrow q, \quad y \to y, \quad \phi \to \frac{\pi}{3} - \phi, \quad \left(\Lambda_1 \leftrightarrow \Lambda_3{}^{-1}, \quad \Lambda_2 \to \Lambda_2{}^{-1}\right), \tag{58}$$

$$p \leftrightarrow q, \quad y \to y, \quad \phi \to \frac{\pi}{3} + \phi, \quad \left(\Lambda_2 \leftrightarrow \Lambda_3{}^{-1}, \quad \Lambda_1 \to \Lambda_1{}^{-1}\right). \tag{59}$$

The second of the above symmetries was already discussed in the classical case of Ref. [6].

For future purposes it is convenient to rewrite the ratio of the different values of Λ_i in the following way

$$\frac{\Lambda_1}{\Lambda_3} = e^{-y\, \sin\left(\phi+\frac{\pi}{3}\right)}, \quad \frac{\Lambda_2}{\Lambda_3} = e^{-y\, \sin\left(\frac{\pi}{3}-\phi\right)}, \quad \frac{\Lambda_1}{\Lambda_2} = e^{-y\, \sin\phi}, \tag{60}$$

7 The phases of the system

The free energy βF of the system, given by Eq. (47), is a function of five variables; $\beta F = \beta F(T, p, q, y, \phi)$. The absolute minimum conditions (46), which correspond to two equations

in our case, allow us to find $y = y(T, p, q)$ and $\phi = \phi(T, p, q)$ for equilibrium, thus selecting the particular phase which is energetically favourable. This calculation is made numerically, and these results determine all the remaining thermodynamic properties of the system. The entropy, energy and specific heat can be subsequently calculated by using the expressions (48). The general behavior of the specific heat, as a function of temperature is presented in Fig. 1. Here we have labelled by T_b, T_u, the transition temperatures between the biaxial-uniaxial phase and the uniaxial-isotropic phase, respectively. Since we are only considering the description of the orientational modes of the system, the thermodynamic quantities associated with the isotropic phase will all be zero.

7.1 The T → 0 (y → ∞) case.

Let us consider the interval $0 < \phi < \frac{\pi}{3}$ in such a way that all the ratios (60) tend to zero exponentially. The corresponding limit in the partition function is taken from (105), by observing that each of the polynomials F_1 can be approximated as

$$F_1(q; \Lambda_2, \Lambda_3) \approx \Lambda_3{}^q \left(1 + \frac{\Lambda_2}{\Lambda_3}\right). \tag{61}$$

In this way, the product of two F's in each term of the partition function factors out, leaving an additional term $F_1(q; \Lambda_1, \Lambda_2)$, which is also approximated in the way of Eq.(61). The final expression for the logarithm of the partition function is

$$\ln Z_0^{(p,q)} = (p+q)\ln\Lambda_3 + q\ln\Lambda_2 + \frac{\Lambda_1}{\Lambda_3} + \frac{\Lambda_2}{\Lambda_3} + \frac{\Lambda_1}{\Lambda_2}. \tag{62}$$

In order to determine which of the last three terms in the above expression dominates, we still have to consider the further intervals $0 < \phi < \frac{\pi}{6}$, where $\sin\phi < \sin(\frac{\pi}{3} - \phi) < \sin(\frac{\pi}{3} + \phi)$, together with $\frac{\pi}{6} < \phi < \frac{\pi}{3}$, where $\sin(\frac{\pi}{3} - \phi) < \sin\phi < \sin(\frac{\pi}{3} + \phi)$. In the first case, the free energy reduces to

$$\beta F = -(p+q)\frac{y}{\sqrt{3}}\cos\phi - q\frac{y}{\sqrt{3}}\cos(\phi - \frac{2\pi}{3}) - e^{-y\sin\phi} + \frac{1}{8}Ty^2, \tag{63}$$

because the term $\frac{\Lambda_1}{\Lambda_2}$ dominates over the remaining fractions in (62). Introducing the notation

$$A(\phi) = \frac{p+q}{\sqrt{3}}\cos\phi + \frac{q}{\sqrt{3}}\cos(\phi - \frac{2\pi}{3}),$$
$$B(\phi) = \frac{p+q}{\sqrt{3}}\sin\phi + \frac{q}{\sqrt{3}}\sin(\phi - \frac{2\pi}{3}), \tag{64}$$

the equations that minimize the free energy are

$$-A(\phi) + \frac{1}{4}Ty + \sin\phi \, e^{-y\sin\phi} = 0,$$
$$B(\phi) + \cos\phi \, e^{-y\sin\phi} = 0. \tag{65}$$

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The above equations are solved by

$$\phi = \phi_0 - \frac{\cos\phi_0}{A(\phi_0)}\mathrm{e}^{-\frac{4A(\phi_0)}{T}\sin\phi_0}, \quad \tan\phi_0 = \frac{\sqrt{3}q}{2p+q},$$
$$y = \frac{4}{T}\left(A(\phi_0) - \sin\phi_0 \ \mathrm{e}^{-\frac{4A(\phi_0)}{T}\sin\phi_0}\right). \tag{66}$$

The solution in the interval $\frac{\pi}{6} < \phi < \frac{\pi}{3}$ is

$$\phi = \phi_0 - \frac{\cos(\frac{\pi}{3}-\phi_0)}{A(\phi_0)}\mathrm{e}^{-\frac{4A(\phi_0)}{T}\sin(\frac{\pi}{3}-\phi_0)}, \quad \tan\phi_0 = \frac{\sqrt{3}q}{2p+q},$$
$$y = \frac{4}{T}\left(A(\phi_0) - \sin(\tfrac{\pi}{3} - \phi_0) \ \mathrm{e}^{-\frac{4A(\phi_0)}{T}\sin(\frac{\pi}{3}-\phi_0)}\right). \tag{67}$$

This limit clearly corresponds to the biaxial equilibrium phase since $\lambda \neq 0, \phi \neq 0$. For the case $0 < \phi < \frac{\pi}{6}$, we obtain the following expression for the specific heat

$$\frac{\mathrm{C}}{\mathrm{k}} = \left(\frac{2q}{T}\right)^2 \mathrm{e}^{-\frac{2q}{T}}, \tag{68}$$

where there is a mass gap given by $2q$. The prediction (68) has to be compared with the classical case, where the specific heat goes like $\frac{\mathrm{C}}{\mathrm{k}} = 3 + \frac{3T}{(\mu \ \sin 3\psi)^2}$ in that limit. Moreover, Eq.(68) signals a peculiar behavior for the cases $q = 0, \ p \neq 0$, which will be separately discussed in section 7.4.

The solution (67) in the interval $\frac{\pi}{6} \leq \phi \leq \frac{\pi}{3}$ leads to

$$\frac{\mathrm{C}}{\mathrm{k}} = \left(\frac{2p}{T}\right)^2 \mathrm{e}^{-\frac{2p}{T}}, \tag{69}$$

for the specific heat in the $T \rightarrow 0$ limit. This is consistent with the symmetry $p \leftrightarrow q$ which connects the corresponding two intervals of ϕ.

7.2   Biaxial-Uniaxial phase transition

The uniaxial phase is characterized by $\lambda \neq 0, \phi = 0$. In order to determine the transition temperatute T_b, we expand the free energy $F(T, \lambda, \phi)$ in powers of ϕ and find the corresponding minimum. The expansion is

$$\beta F(T, \lambda, \phi) = f(z) - 6z + 6 \ Tz^2 + (z^2 g(z) + z \ h(z))\phi^2 + \mathrm{O}(\phi^4), \tag{70}$$

where the functions f, g, h are explicitly known and $z = \frac{\lambda}{T}$. The partition function is invariant under the change $\phi \rightarrow -\phi$, which is reflected in the above expansion. To determine the transition temperature we approach from the biaxial phase and look for the corresponding minimum of (70) having $\lambda \neq 0, \ \phi \neq 0$, but small. The conditions are

$$0 = \frac{\partial F}{\partial \phi} = 2\phi z \left[\lambda g(z) + Th(z)\right] + \mathrm{O}(\phi^3), \tag{71}$$

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$$0 = \frac{\partial F}{\partial \lambda} = \frac{\partial f(z)}{\partial z} - 6 + 12\lambda + O(\phi^2). \tag{72}$$

From Eq.(71) we obtain $\bar{z}g(\bar{z}) + h(\bar{z}) = 0$, which numerical solution determines $\bar{z} = \frac{\lambda_b}{T_b}$. Substituting this result in Eq.(72) the transition temperature results in

$$T_b = \frac{1}{12\bar{z}} \left(6 - \frac{\partial f(\bar{z})}{\partial \bar{z}}\right). \tag{73}$$

Some results, for different values of p and q, are presented in Table I. In this table, the parameters μ and ψ corresponding to the quantum numbers p and q are obtained from Eqs. (18), (19) and (25) The fifth column is obtained from Eq. (73). The next column shows the conversion to the classical temperature, according to Eq. (37). The predictions of the classical model are presented in the last column.

7.3   Uniaxial-Isotropic phase transition

As we keep increasing the temperature we go from the uniaxial phase to the isotropic phase characterized by $\phi = 0, \lambda = 0$. To determine the transition temperature T_u we proceed in complete analogy to the previous section. Now we expand the free energy of the uniaxial phase in the vicinity of $z = 0$,

$$\beta F(z, \phi = 0, T) = -\ln Z_0^{(p,q)} + \frac{3}{2}T\sigma^2 = 6\,Tz^2 - 3I_2 z^2 - \frac{12}{5}I_3 z^3$$
$$-\ln\frac{(p+1)(q+1)(p+q+2)}{2} + \frac{9}{10}I_2(I_2 + 2)z^4 + \frac{108}{35}I_2 I_3 z^5 + O(z^6), \tag{74}$$

where we recall that $z = \frac{\lambda}{T}$.

The extremum condition $\frac{\partial F}{\partial \sigma} = 0$ requires $3T\sigma = \frac{\partial \ln Z_0^{(p,q)}}{\partial \sigma}$. The general form of $\frac{\partial \ln Z_0^{(p,q)}}{\partial \sigma}$ as a function of σ is presented in Fig. 2. From here it is clear that the transition temperature is given by the slope of the straight line which is tangent to this curve, i.e. there is a critical temperature beyond which it is not possible to satisfy the consistency conditions. This implies the further condition $3T = \frac{\partial^2 \ln Z_0^{(p,q)}}{\partial \sigma^2}$. Both requirements imply that one is looking for an inflexion point of the free energy (74): $\frac{\partial F}{\partial \sigma} = 0$, $\frac{\partial^2 F}{\partial \sigma^2} = 0$.

Keeping up to fourth order terms in (74), the above system is solved by

$$z^* = \frac{I_3}{I_2(I_2 + 2)}, \quad T^* = \frac{1}{2}I_2 + \frac{3}{10}\frac{I_3^2}{I_2(I_2 + 2)}. \tag{75}$$

This solution is a good aproximation whenever z^* is small.

Nevertheless, for a range of temperatures below T^*, we can verify that the uniaxial phase does not provide an absolute minimum for the free energy of the system. In fact, the calculated free energy is higher than the one corresponding to the isotropic phase, which

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makes the uniaxial phase metastable. In this way, the true transition temperature T_u between the uniaxial and the isotropic phase is obtained by the minimum condition together with the requiremente that $\beta F = \beta F|_{\text{isotropic}} = -\ln\frac{1}{2}(p+1)(q+1)(p+q+2)$. In the same approximation as the one used in Eq.(75), these new conditions provide

$$z_u = \frac{4I_3}{3I_2(I_2+2)}, \quad T_u = \frac{1}{2}I_2 + \frac{4}{15}\frac{I_3^2}{I_2(I_2+2)}, \tag{76}$$

which confirm that $T_u < T^*$ together with the fact that the metastable region is small indeed. A further discussion of the metastability region can be found in section 4.5 of Ref. [2]

We can calculate the limit of the specific heat when we approach T_u fom the left, in the case when $I_3 \to 0$ ($p \to q$). To this end we have to find $z = z(T)$, which we obtain by requiring $\frac{\partial F}{\partial z} = 0$ in Eq.(74). We get

$$z = \frac{1}{I_2(I_2+2)}\left(I_3 + \sqrt{I_3^2 + \frac{10}{3}I_2(I_2+2)(\frac{I_2}{2} - T)}\right). \tag{77}$$

From the above equation we can verify that if we substitute the value for T_u given by Eq.(76), we recover the value z_u written in the same equation. Next we use the expression (48) for the specific heat to obtain

$$\frac{C}{k}|_{T \to T_u} = 20\frac{I_2}{I_2+2} + O(I_3^2). \tag{78}$$

This expression has the correct classical limit given by $\frac{C}{k}|_{T \to T_u} = 20$.

The above results (75), (76) can be further refined by taking into account the term z^5 en the expression (74). Some numerical results are presented in Table II, for different values of p and q. The fourth columm gives the quantum prediction for the transition temperature T_u, which is subsequently converted to the classical temperature in the fifth column. The last columm contains the classical predictions.

7.4 The $q = 0, p \neq 0$ case

As we will see in the sequel, this situation has no counterpart in the classical description because here we have only an isotropic-uniaxial transition and the biaxial phase is not present.

Let us consider the limit $T \to 0$ within the range $0 \leq \phi \leq \frac{\pi}{6}$ in the expression (103) for the exact partition function. As before, $\Lambda_1, \Lambda_2 \to 0$ while $\Lambda_3 \to \infty$ in such a way that the expansion of the partition function up to second order terms leads to

$$\ln Z_0^{(p,q=0)} = p\,\ln\Lambda_3 + \frac{\Lambda_1}{\Lambda_3} + \frac{\Lambda_2}{\Lambda_3} - \frac{1}{2}\left(\frac{\Lambda_1}{\Lambda_3}\right)^2 - \frac{1}{2}\left(\frac{\Lambda_2}{\Lambda_3}\right)^2 + \dots. \tag{79}$$

The above expression differs from the $q = 0$ restriction of Eq. (62), in the absence of the previously dominating term $\frac{\Lambda_1}{\Lambda_2}$. This is because one has to take the $q = 0$ value in

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the full expression and not in a truncation of it. For example, $F_1(q = 0; u, v) = 1$, but in an approximation where $u \geq v$, we can write $F_1 = u^q(1 + \frac{v}{u} + \ldots)$, which will lead to $F_1(q = 0; u, v) = (1 + \frac{v}{u} + \ldots)$. It is enough to consider the expression (79) to first order, which leads to

$$\beta F = -\frac{p}{\sqrt{3}} y \cos\phi - e^{-y\sin(\frac{\pi}{3} - \phi)} - e^{-y\sin(\frac{\pi}{3} + \phi)} + \frac{1}{8} T y^2. \tag{80}$$

Since we are interested in solutions near $\phi = 0$, we have to keep both exponentials, which are of the same order now. The conditions for a minimum of the free energy are

$$\frac{1}{4} T y = \frac{p}{\sqrt{3}} \cos\phi - \sin(\frac{\pi}{3} - \phi) e^{-y\sin(\frac{\pi}{3} - \phi)} - \sin(\frac{\pi}{3} + \phi) e^{-y\sin(\frac{\pi}{3} + \phi)} \tag{81}$$

$$\sin\phi = \frac{\sqrt{3}}{p} \left(\cos(\frac{\pi}{3} + \phi) e^{-y\sin(\frac{\pi}{3} + \phi)} - \cos(\frac{\pi}{3} - \phi) e^{-y\sin(\frac{\pi}{3} - \phi)} \right) := H(\phi). \tag{82}$$

In writing the last equation we are assuming that $y \neq 0$. We have that $H(\phi = 0) = 0$ and it is a direct matter to show that $\frac{dH}{d\phi} < 0$, within the interval under consideration. This means that the only solution to Eq.(82) is $\phi = 0$, i.e. we remain in the uniaxial phase for low temperatures, with no transition to the biaxial one. The remaining equilibrium condition is

$$y = \frac{4}{T\sqrt{3}} \left(p - 3e^{-\frac{2p}{T}} \right). \tag{83}$$

The above expression leads to a specific heat given by

$$\frac{C}{k} = \frac{8p^2}{T^2} e^{-\frac{2p}{T}}, \tag{84}$$

in the $T \to 0, y \to \infty$ limit.

The absence of the biaxial phase in this case can also be verified from the general discussion of section 7.2, by looking at the expansion of the free energy in powers of ϕ. It is possible to verify numerically that the coefficient of the power ϕ^2 in Eq. (70) cannot be made zero, unless $z = 0$. That is to say, there can be no transition to the biaxial phase when $q = 0, \ p \neq 0$.

Another piece of information related to the above statement is the calculation of the angle ψ. The general result is

$$\cos 3\psi = \frac{p(p + 3)(2p + 3)}{2(p^2 + 3p + 3)^{\frac{3}{2}}}. \tag{85}$$

Now, in the limit $p \to \infty$, we recover the classical regime together with the fact that $\cos 3\psi = 1$, i. e. $\psi = 0$. Recalling the phase diagram of Ref.[6], we verify that in this regime we have only the uniaxial and isotropic phases.

7.5 The $p = q$ case

Here $I_2 = p(p+2)$, $I_3 = 0$. The specific heat, together with the entropy are shown in Figs. 5 and 8, as a function of temperature. All the points correspond to the biaxial phase and, exactly as in the classical situation, the phase transition is directly to the isotropic one. In order to better understand the limiting values of the transition temperature, together with the resulting specific heats, we we will take the corresponding limit starting from the uniaxial phase, with $I_3 = 0$. In this case Eq. (77), valid for any point in this phase, reduces to

$$z = \sqrt{\frac{10}{3 \; I_2(I_2 + 2)}(\frac{I_2}{2} - T)}. \tag{86}$$

From Eqs.(76) we see that, in this limit, the uniaxial phase merges into the isotropic one, with $z = 0$, at the transition temperature $T_b = T_u = \tilde{T} = \frac{I_2}{2}$. In the conventions of Ref. [6], this temperature corresponds to

$$\tilde{T}_c = \frac{1}{8}\frac{I_2}{I_2 + 1}, \tag{87}$$

which reproduces the value $\tilde{T}_c = \frac{1}{8}$ for high quantum numbers. The specifc heat at the transition is

$$\frac{C}{k}\Big|_{\tilde{T}} = 5 \; \frac{I_2}{I_2 + 2} = 5 \; \frac{(p+1)^2 - 1}{(p+1)^2 + 1}. \tag{88}$$

The above result reproduces the classical prediction.

Let us observe that Eq.(86) makes sense only when $T \leq \frac{I_2}{2}$. In other words, we really approach the transition point from the sector of the uniaxial phase which has the biaxial phase as a boundary.

7.6 The order parameters of the system

In the classical case, the order parameters corresponding to the uniaxial and biaxial phases, respectively, are defined by [6]

$$U = Tx\frac{\cos\phi}{\cos\psi} = \frac{2}{\beta J}\frac{\lambda_c \cos\phi}{\mu \cos\psi}, \qquad B = Tx\frac{\sin\phi}{\sin\psi} = \frac{2}{\beta J}\frac{\lambda_c \sin\phi}{\mu \sin\psi}, \tag{89}$$

where λ_c refers to the notation in this reference. The above definitions are such that $U \neq 0$, when $T \leq T_u$ and $B \neq 0$ when $T \leq T_b$.

Considering that

$$\rho = -\frac{2\sqrt{3}}{T}\lambda \sin\phi \qquad \sigma = -\frac{2}{T}\lambda \cos\phi, \tag{90}$$

with $T = \frac{4}{\beta J}$ and $\lambda_c = \beta J \lambda$, the corresponding order parameters in the quantum case can be taken as

$$U = -\frac{T\sigma}{\mu \cos\psi}, \qquad B = -\frac{T\rho}{\sqrt{3}\mu \sin\psi}, \tag{91}$$

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in order to reproduce the classical quantities in the apropriate limit. Let us recall that μ and ψ are related to p and q through the equations (18), (19) and (25). Two complementary examples are presented in Figs. 10 and 11. The former corresponds practically to the classical situation, while the latter refers to a lower lying quantum state.

8   Final Comments and Conclusions

We have presented a quantum mechanical description of the orientational degrees of freedom of a biaxial nematic liquid in the mean field approximation, thus extending the classical approach proposed in Ref. [6].

The fact that the dynamical variables carry a representation of $SU(3)$ allows for an exact calculation of the quantum partition function, in terms of the Weyl formula for the characters of the group. In this way, the consistence equations of the mean field approximation reduce to two coupled algebraic equations, in a manner similar to the case in Ref. [6].The work presented here constitute a nice example of the applications of group theory techniques to quantum statistical mechanics. As expected [13, 14], the classical behavior is recovered in the high temperature, high quantum numbers regime. In general, the discrepancies between the two approaches begin to appear at temperatures which are lower that the biaxial-uniaxial transition temperature.

Under these circumstances and considering the actual state of the art in the production of liquid crystals, the liquid will probably crystalize and these effects will be irrelevant from the experimental point of view, in the case of the nematic phase under present-day laboratory conditions. This emphasizes the fact that the classical approximation is very adequate for the description of the phase transitions in this model. Nevertheless, further technical developments may lead to nematic liquids with substantially lower transition temperatures, such that quantum effects might turn to be important. Also, it is necessary to continue exploring the relevance and description of liquid crystals in high density-high temperature nuclear matter.

The general phase structure of the system includes: a biaxial phase in the range $0 < T < T_b$, a uniaxial phase in the range $T_b < T < T_u$, $T_b < T_u$, and an isotropic phase for $T > T_u$. This last phase acts here as a reference, because the model does not include a description of translational degrees of freedom of the liquid. This structure is exhibited in Figs. 3, 4 and 5 (for the specfic heat) together with Figs. 7 and 9 (for the entropy). The specific heat always presents a discontinuity at T_b, while the entropy remains continuous there. This corresponds to a second order phase transition. We expect the same behavior at the temperature T_u, since both phase transitions are associated to symmetry changes in the liquid. The temperatures of the different phase transitions in the quantum calculation are about $15 - 30$ % lower than the classical situation, in the most unfavourable cases (low quantum numbers).

In the low temperature limit $T \to 0$, the quantum calculation of the specific heat leads to the result $\frac{C}{k} \sim \frac{1}{T^2} e^{-\frac{\alpha}{T}}$, according to Eqs. (68) and (69), signaling a mass gap characteristic

of the quantum spectra. The classical limit in this regime is $\frac{C}{k} = 3$. Also, the quantum calculation is consistent with the Nernst postulate for the entropy in the $T \to 0$ limit.

Deviations from the above general picture are present in two cases: (i) the region $p = q$ produces a direct transition from the biaxial to the isotropic phase, in complete analogy with the classical situation. This is shown in Figs. 5 and 8. (ii) the region $q = 0$, $p \neq 0$ ($p = 0$, $q \neq 0$) does not support the biaxial phase and only allows for a uniaxial-isotropic phase transition. This whole quantum region is the analogous to the $\psi = 0, (\psi = \frac{\pi}{3})$ limit in the classical case. These values for ψ are not allowed in the quantum regime, leading to $q = -1$ ($p = -1$).

Our ultimate goal, which is not discussed in this work, would be to incorporate spin (magnetic moment) degrees of freedom into the model for the nematic liquid, in order to study how the thermodynamic phases and equilibrium parameters are modified . Following an analogous line of development, this would require the introduction of a supergroup as a way of characterizing the underlying orientational degrees of freedom. In this case it would be also interesting to study the classical limit of the quantum version. This limit will shed some light into the role of the supersymmetric extension [16] of the Harish-Chandra, Itzykson - Zuber (HCIZ) integral, in the classical description of the model. A direct classical calculation of the supersymmetric model, along the lines of Ref.[6], presents some difficulties, even though the corresponding HCIZ integral is known [16] . In fact, there is no Macfarlane's theorem in this case and the interpretation of the Grassmann numbers that naturally arise is not at all clear. In this situation, we expect the quantum calculation to be free of these ambiguities, besides of providing the complete and correct answer to the problem.

Acknowledgements

The Appendix

Any set of hermitian operators S_a, $a = 1, 2, \ldots, 8$ satisfiying the commutators

$$[S_a, \ S_b] = if_{abc}S_c, \tag{92}$$

with f_{abc} being the $SU(3)$ structure constants carry a representation of the group

The fundamental representation of $SU(3)$ is provided by the Gell-Mann λ_a matrices

$$\lambda_1 = \tfrac{1}{2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \ \lambda_2 = \tfrac{1}{2}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \ \lambda_3 = \tfrac{1}{2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\lambda_4 = \tfrac{1}{2}\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \ \lambda_5 = \tfrac{1}{2}\begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}, \ \lambda_6 = \tfrac{1}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$\lambda_7 = \tfrac{1}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \ \lambda_8 = \tfrac{1}{2\sqrt{3}}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix},$$

which are traceless and satisfy $[\lambda_a, \lambda_b] = if_{abc}\lambda_c$. The explicit expression for the $SU(3)$ structure constants is given by

$$f_{abc} = -2itr([\lambda_b, \ \lambda_c] \ \lambda_a) \tag{93}$$

.and they are completely antisymmetric in any pair of indices. The Gell-Mann matrices also satify

$$\{\lambda_a, \ \lambda_b\} = \frac{1}{3}\delta_{ab}\mathbf{I} + d_{abc} \ \lambda_c, \tag{94}$$

where d_{abc} are completely symmetric in any pair of indices.

The adjoint representation of $SU(3)$ has dimension eight and possesses two invariant tensors

$$\delta_{ab} = 2tr(\lambda_a\lambda_b), \qquad d_{abc} = 2tr(\{\lambda_b, \lambda_c\}\lambda_a). \tag{95}$$

The irreducible representations of $SU(3)$ are labeled by two integers (p, q) where $p + q$ denotes the number of boxes in the first row and q denotes the number of boxes in the second row, of the associated Young tableaux. The dimension D of the (p, q) representation is

$$D^{(p,q)} = \frac{1}{2}(p + q + 2)(p + 1)(q + 1). \tag{96}$$

The weights of the fundamental representation are

$$\vec{\mu}_1 = \left(\frac{1}{2}, \frac{1}{2\sqrt{3}}\right), \quad \vec{\mu}_2 = \left(-\frac{1}{2}, \frac{1}{2\sqrt{3}}\right), \quad \vec{\mu}_3 = \left(0, -\frac{1}{\sqrt{3}}\right), \tag{97}$$

which denote de λ_3, λ_8 eigenvalues respectively.

In the course of this research, sometimes it has proved useful to rewrite the partition function (49) introduccing some standard polynomial functions, like $F_1(k; u, v)$

$$u^{k+1} - v^{k+1} = (u - v) \sum_{j=0}^{k} u^j v^{k-j} := (u - v) F_1(k; u, v), \tag{98}$$

together with $F_2(k; u, v, w)$,

$$F_1(k; u, v) - F_1(k; u, w) := (v - w) F_2(k - 1; u, v, w), \tag{99}$$

which leads to the more explicit form

$$F_2(k; u, v, w) = \sum_{i=0}^{k} u^i F_1(k - i; v, w) = \sum_{i=0}^{k} u^{k-i} F_1(i; v, w). \tag{100}$$

In general, for higher values of the subindex $n = 3, 4, \ldots$, the corrresponding polynomials can be defined inductively by

$$F_n(k; u, v, w, \ldots) = \sum_{i=0}^{k} u^i F_{n-1}(k - i; v, w, \ldots). \tag{101}$$

Some of the properties of the F's are the following:
(i) They are completely symmetric with respect to the exchange of any two arguments.
(ii) The difference between two F's which differ in just one argument is given by

$$F_n(k; u_1, \ldots, u_n, u_{n+1}) - F_n(k; u_1, \ldots, u_n, u_{n+2})$$
$$= (u_{n+1} - u_{n+2}) F_{n+1}(k - 1; u_1, \ldots, u_n, u_{n+1}, u_{n+2}). \tag{102}$$

In terms of the above polynomials F_1 and F_2, different cases of the partition function (49) are written as follows

$$Z_0^{(p,q=0)} = F_2(p; \Lambda_1, \Lambda_2, \Lambda_3). \tag{103}$$

$$Z_0^{(p=q)} = F_1(p; \Lambda_1, \Lambda_2) F_1(p; \Lambda_2, \Lambda_3) F_1(p; \Lambda_1, \Lambda_3) \tag{104}$$

$$Z_0^{(p,q)} = \frac{1}{\Lambda_1 - \Lambda_2} \left(\Lambda_1^{q+1} F_1(q; \Lambda_2, \Lambda_3) F_1(p; \Lambda_1, \Lambda_3) - \right.$$
$$\left. \Lambda_2^{q+1} F_1(q; \Lambda_1, \Lambda_3) F_1(p; \Lambda_2, \Lambda_3) \right) \tag{105}$$

$$Z_0^{(p,q)} = \sum_{j=0}^{q} \sum_{k=0}^{p} \Lambda_3^{j+k} (\Lambda_1 \Lambda_2)^{q-j} F_1(p + j - k; \Lambda_1, \Lambda_2). \tag{106}$$

Some explicit expressions of the F's polynomials are the following

$$F_1(1; u, v) = u + v, \quad F_1(2; u, v) = u^2 + uv + v^2,$$
$$F_1(3; u, v) = u^3 + u^2 v + uv^2 + v^3, \tag{107}$$

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$$
\begin{aligned}
F_2(1; u, v, w) &= u + v + w, \\
F_2(2; u, v, w) &= u^2 + u^2 + w^2 + uv + uw + vw, \\
F_2(3; u, v, w) &= u^3 + v^3 + w^3 + u^2(v + w) + v^2(u + w) + w^2(u + v) \\
&\quad + uvw.
\end{aligned}
\tag{108}
$$

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Figure Captions

Fig. 1 General form of the specific heat as a function of temperature, for the different phases.

Fig. 2 General form of $\frac{\partial \ln Z_0^{(p,q)}}{\partial \sigma}$ as a function of σ, for $\lambda = 0$.

Fig. 3 Specific heat for $p = 17$, $q = 48 \longleftrightarrow \mu = 40.0$, $\psi = 45.0^o$. The upper curve is the classical result. The temperature is in classical units.

Fig. 4 Specific heat for $p = 25$, $q = 30 \longleftrightarrow \mu = 33.0$, $\psi = 33.0^o$. The upper curve is the classical result. The temperature is in classical units.

Fig. 5 Specific heat for different values of $p = q \longleftrightarrow \psi = 30.0^o$, different values of μ. The upper curve is the classical result. The temperature is in classical units.

Fig. 6 Specific heat for $p = 1 \ q = 2 \longleftrightarrow \mu = 2, 9 \ \psi = 36.6^o$ and $p = 27$, $q = 41 \longleftrightarrow \mu = 40.7 \ \psi = 36.6^o$. The upper curve is the classical result. The temperature is in classical units.

Fig. 7 Quantum entropy for $p = 25$, $q = 30$.

Fig. 8 Quantum entropy for $p = q$. The temperature is in classical units.

Fig. 9 Quantum entropy for $p = 1 \ q = 2$ and $p = 27 \ q = 41$. The temperature is in classical units.

Fig. 10 Quantum order parameters for $p = 27$, $q = 41$.

**Fig. 11** Quantum order parameters for $p = 1$, $q = 2$.
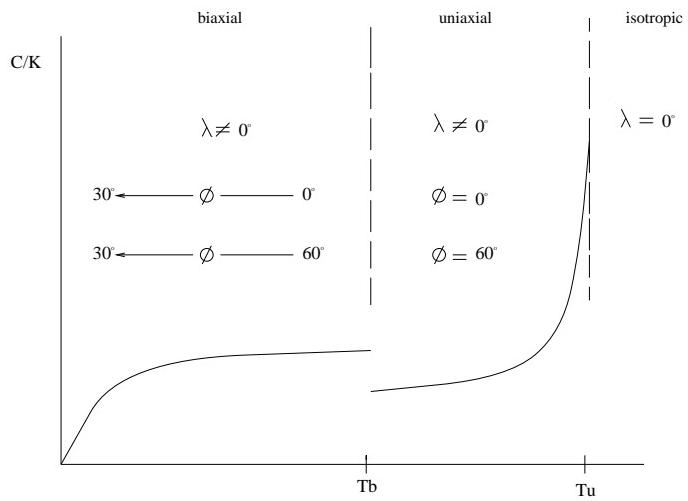
Fig. 1

Fig. 2

Fig. 3

Fig. 4

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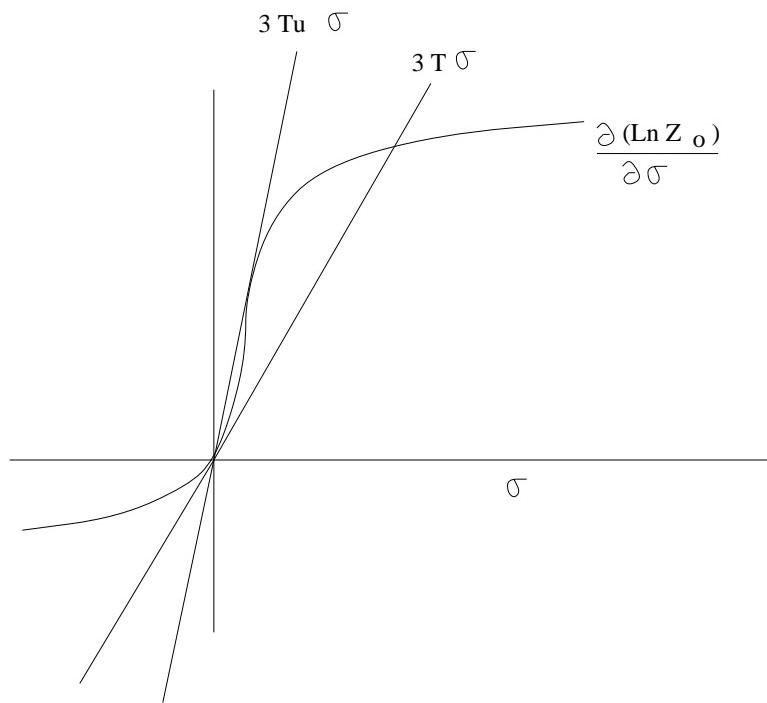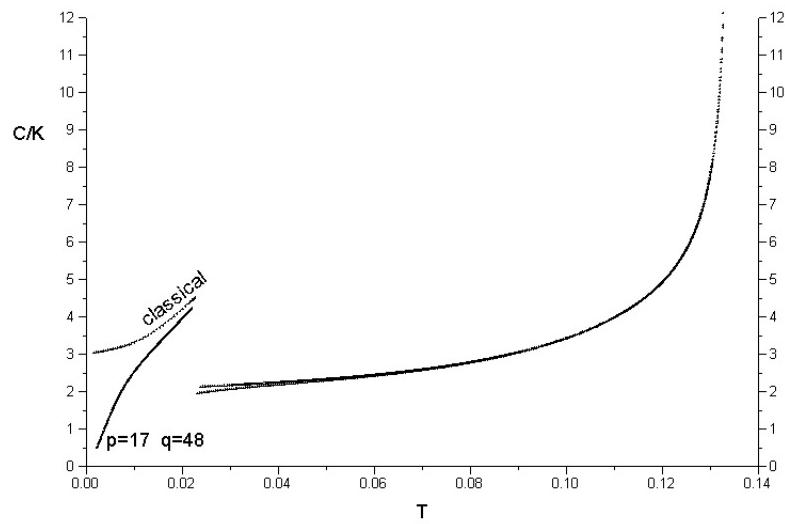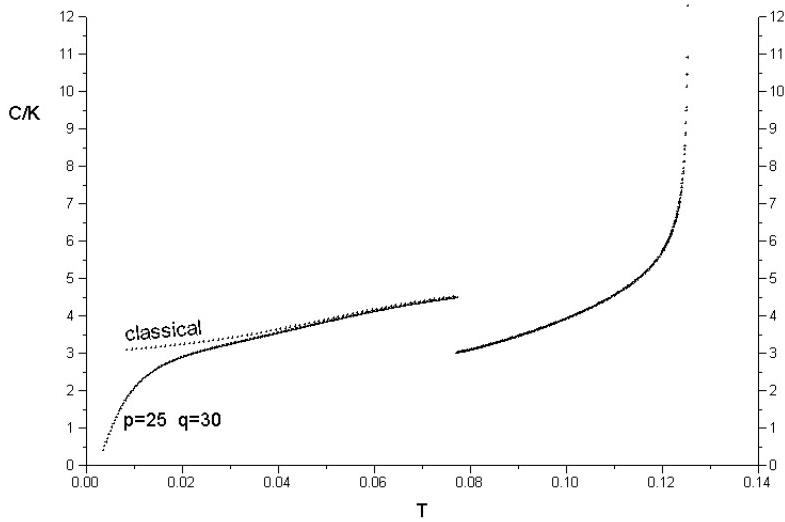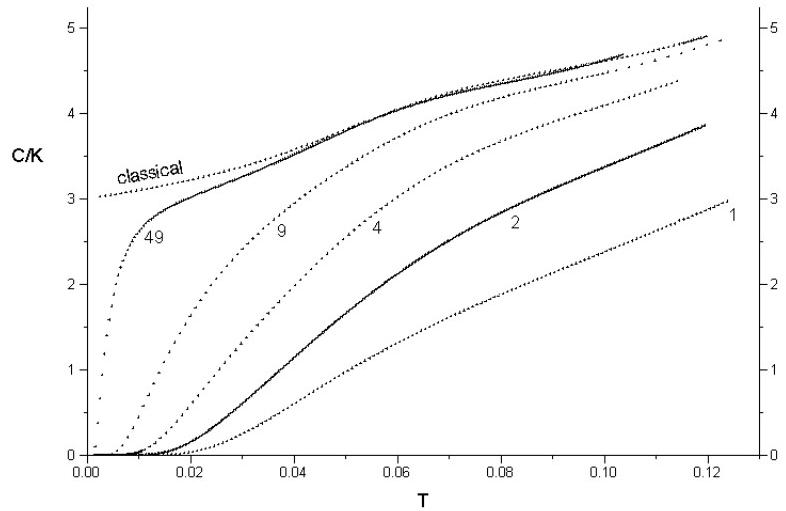
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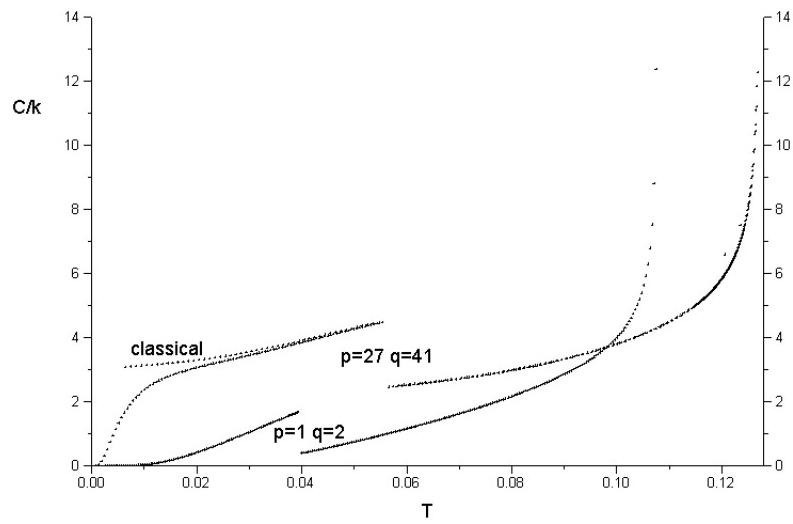
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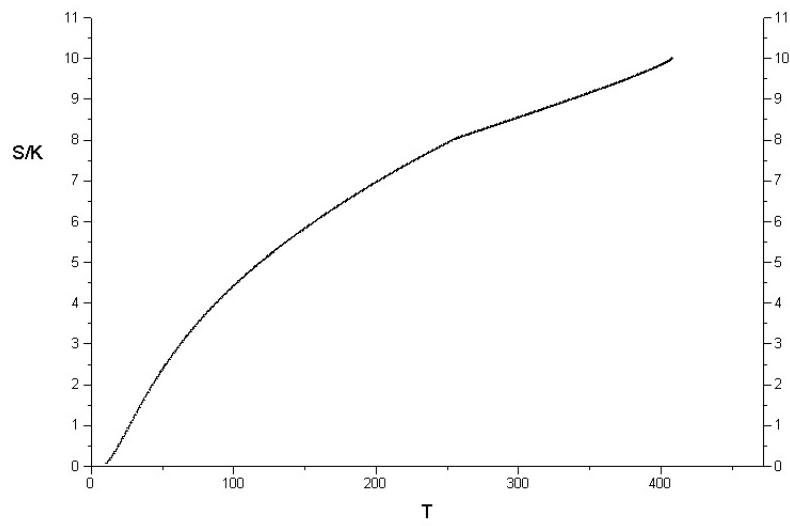
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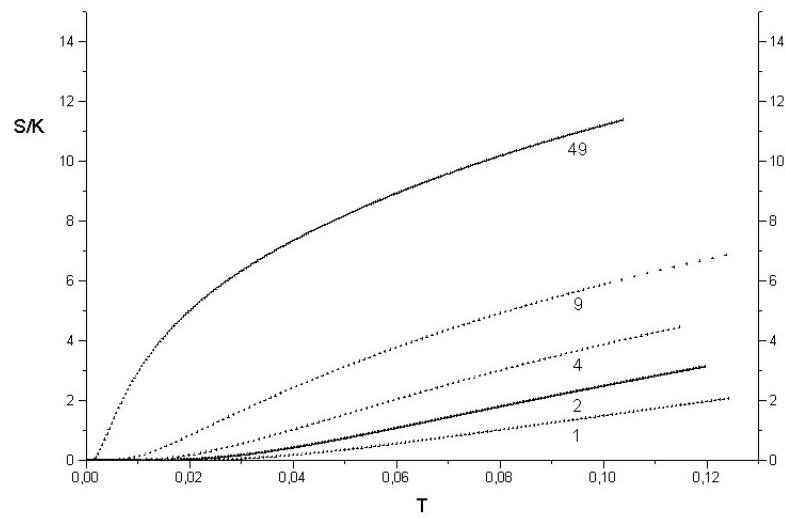
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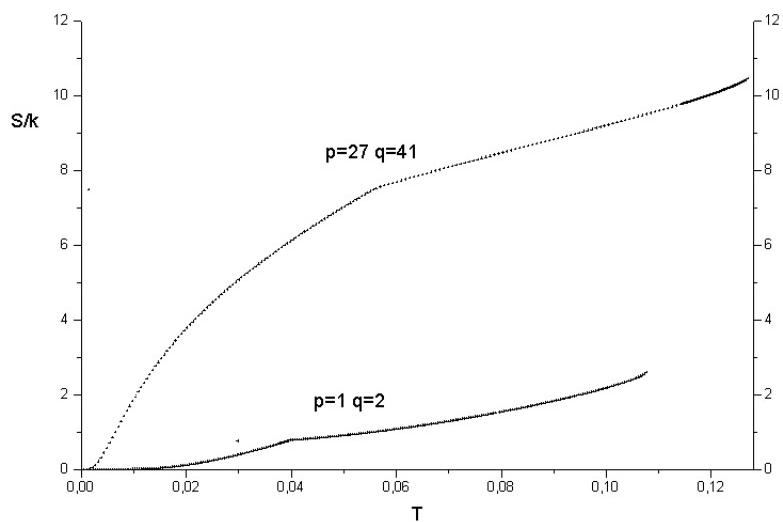
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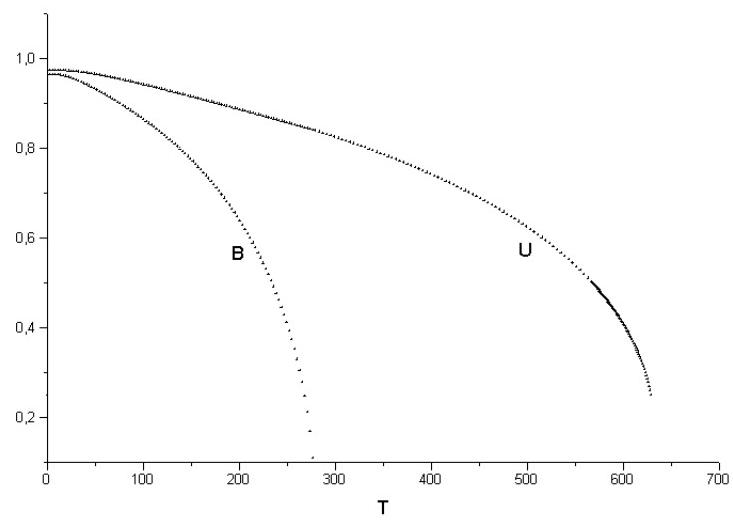
Fig. 10
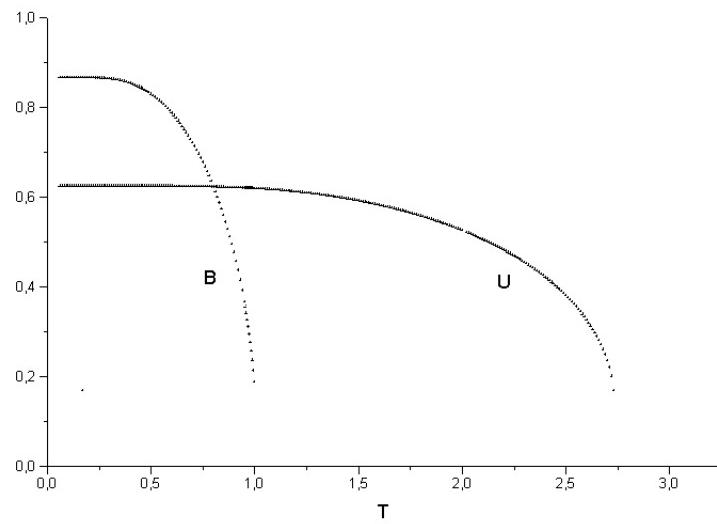
Fig. 11

Table I

p	q	μ	ψ	T_b	$\rightarrow$	$(T_b)_c$	T_b(classical)
2	24	$\frac{2}{3}\sqrt{709}$	54.4	2.667		0.00282	0.00317
4	43	$\frac{2}{3}\sqrt{2181}$	54.7	8.000		0.00275	0.00287
17	48	$\frac{2}{3}\sqrt{3607}$	45.0	109.5		0.02277	0.02286
1	2	$\frac{2}{3}\sqrt{19}$	36.6	1.015		0.04008	0.05614
27	41	$\frac{28}{3}\sqrt{19}$	36.6	278.3		0.05605	0.05614
27	47	$\frac{8}{3}\sqrt{277}$	38.6	273.5		0.04628	0.04632
25	30	$\frac{2}{3}\sqrt{2443}$	32.9	256.1		0.07862	0.07877

Table II

p	q	ψ	T_u	$\rightarrow$	$(T_u)_c$	T_u(classical)
2	24	54.4	129.5		0.1370	0.1454
4	43	54.7	383.2		0.1318	0.1455
17	48	45.0	637.8		0.1326	0.1361
1	2	36.6	2.725		0.1076	0.1275
27	41	36.6	631.8		0.1272	0.1275
27	47	38.6	760.5		0.1287	0.1292
25	30	32.9	408.2		0.1253	0.1255